

BACKGROUND OF THE INVENTION

5 The present invention relates to a method of
manufacturing an optical element, including a step of
machining and washing a substrate made of CaF_2 single
crystalline or the like, an exposure apparatus using
the optical element, and the optical element washing
0 machine. In particular, the present invention relates
to a method of manufacturing a fluorine lens which is
used in the case where a high function is required,
which is cut from a CaF_2 single crystalline substrate
and machined, and has a large aperture and high profile
5 irregularity.

Conventionally, an optical element such as a lens made of a fluoride series crystal material such as CaF_2 or MgF_2 has preferable transmittance in an optical characteristic over an extremely wide wavelength band and low dispersiveness. Thus, this optical element has been used as a high precision lens of which a high function is required, such as a high grade camera lens or a television camera lens.

Also, the optical element such as the lens made of the fluoride series crystal material such as CaF_2 or MgF_2 , has high transmittance with respect to ultraviolet

radiation by an excimer laser. Thus, use of such an optical element is started for various optical elements of an illuminating optical system and those of a projection optical system in a projection exposure apparatus using ultraviolet radiation with a wavelength of about 248 nm (KrF excimer laser), ultraviolet radiation with a wavelength of 193 nm (ArF excimer laser), or ultraviolet radiation with a wavelength of 157 nm (F₂ excimer laser).

10 In manufacturing such kind of lens, generally, a wash solution is poured into a wash bath and then a lens (substrate) which has undergone surface machining is immersed therein. In this state, the lens is washed by an ultrasonic cleaning method or the like to remove a
15 contamination such as an organic material (such as oil) or an inorganic particle (such as abrasive) on the surface of the lens. Thus, the reduction in the transmittance of the lens due to the contamination is prevented.

20 However, it has been found that even if such washing is made, it is still impossible to obtain a lens with predetermined transmittance. One of the reasons is the existence of a deterioration layer on the surface of the substrate, which is produced during
25 the lens machining.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method of manufacturing an optical element capable of obtaining higher transmittance than that of the conventional optical element.

According to the present invention, there is provided a method of manufacturing an optical element, comprising the steps of: machining a substrate; and removing a deterioration layer from the surface of the substrate after the machining.

According to the present invention, since the manufacturing method includes the stage of removing the deterioration layer on the surface of the substrate, the reduction in the transmittance due to the deterioration layer can be completely prevented or greatly suppressed. Thus, a method of manufacturing an optical element capable of obtaining higher transmittance than that of the conventional one, can be provided.

In embodiments described later, after the machining, removing a contamination from a surface of the substrate is provided.

In embodiments described later, although the surface of the substrate is ultrasonic-washed with an aqueous wash solution to etch the deterioration layer on the surface, the etching time of the deterioration layer by this ultrasonic washing is set such that the

00873999-060601

The optical element as a subject of the present invention is a lens, a prism, a transparent plate, a transparent rod, or the like.

25 the focal control unit has basic control value
 setting means for setting a basic control value for a
 focal matching state of the ultraviolet radiation from

the excimer laser unit, focal matching determination means for determining a focal matching state of the excimer laser light, and correction means for sending a correction amount corresponding to a determination result of the focal matching determination means to the position control means.

10 The basic control value setting means is means for setting the basic control value provided to hold the focal matching state of the excimer laser light within an acceptable range. The focal matching determination means is means for determining whether the excimer laser light is focused or not, that is, whether the focal matching state is in the acceptable range or not. The correction means is means for sending a moving
15 amount of the lens in a vertical direction as a correction value to a lens position control means so as to hold the focal matching state within the acceptable range, in the case where the excimer laser light is not focused, that is, in the case where the focal matching
20 state is outside the acceptable range. At this time, a moving speed of the lens in a horizontal direction is determined by the relation to a washing rate. When the lens is moved in the vertical direction and/or the horizontal direction, simultaneously it is again
25 determined whether the excimer laser light is focused or not. The determination of the focal matching state, sending of the correction value based on the

determination result, and moving of the lens in accordance with the correction value are repeated such that the focal matching state of the excimer laser light is always kept. Note that known structures can be applied to the structures of the respective means composing the laser light focal control unit.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

Fig. 1 is a flowchart of a manufacturing method according to the present invention;

Fig. 2 is a schematic view of a lens washing machine used in the present invention; and

Fig. 3 is a schematic view of a projection exposure apparatus using an optical element manufactured by the method of Fig. 1 as an optical system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 is a flowchart of a manufacturing method of the present invention. In the drawing, a part or all of step 1 and step 2 can be simultaneously performed.

One aspect of the present invention is a method of washing a substrate made from a CaF_2 single crystalline substrate, including the steps of; polishing a surface of the CaF_2 single crystalline substrate with a predetermined surface shape, forming on the surface

thereof a protective film, and then washing the substrate, and

this aspect adopts

5 a step of peeling the protective film from the substrate and then immersing the substrate into acetone,

then, a step of taking out the substrate from the acetone and wiping the surface thereof with a paper containing diamond powder,

10 then, a step of processing the surface of the substrate with solvent and then processing the substrate with UV/O₃,

then, a step of ultrasonic-processing the substrate in a wash solution containing a
15 surface-active agent,

a step of ultrasonic-processing the substrate in pure water and then rinsing it with the pure water, and a step of drying the ultrasonic-washed substrate.

Now, in the machining step, first, a rough shape
20 of an optical element is set using a material (CaF₂) of the lens and then a final surface shape and a final surface roughness are determined by polishing the substrate. Thus, a contamination produced in the machining step of the substrate is an inorganic
25 material such as abrasive or foreign matter and an organic material such as oil, fingerprints, or the residue of a protective film. These contaminations are

09873999-066604

produced in respective machining steps by covalent bond, electrostatic force, van der Waals power or the like. Also, there is the case where a machining affecting layer or a deterioration layer can be formed in a minute region near the surface by machining in a polishing step. This deterioration layer becomes a layer for absorbing light with a short wavelength, such as ultraviolet radiation.

Next, after the final surface shape and the final surface roughness of the optical element are determined, an antireflective film for improving the transmittance is formed on the surface of the substrate. Therefore, after the above machining step is completed, a final washing before the formation of the antireflective film becomes very important. In particular, with respect to, for example, a lens for an excimer laser used in lithography of an ultraviolet region, the transmittance approximate to a theoretical value is required. Thus, the final washing after the lens machining becomes very important.

Thus, according to this aspect of the present invention, in order to obtain a sufficient washing effect in the final washing after the lens machining, the above washing step is adopted.

That is, of the organic material residue, the inorganic particle, and the deterioration layer, which are left on the surface of the substrate after the

5

10

25

layer can be removed from the surface of the substrate by the ultrasonic processing with this aqueous wash solution for a predetermined time.

That is, in this aspect, of light absorption
5 layers adhered to the surface of the lens, the organic material residue is removed by the acetone immersing, the wiping with the paper containing diamond powder, and the UV/O₃ processing. The deterioration layer is removed in addition to the inorganic particle by the
10 ultrasonic processing in the aqueous wash solution.

A manufacturing method according to a second aspect of the present invention has, as a stage of removing a contamination from the surface of a
15 substrate while keeping a crystal structure in the surface of a CaF₂ single crystalline substrate, a step of removing the contamination from the surface of the substrate with laser light irradiation, and further includes a stage of ultrasonic-washing the surface of the substrate with an aqueous wash solution.

20 As described above, in a machining step, first, an optical element substrate with a rough shape is cut from a material. Then, a final surface shape and a final surface roughness are obtained by polishing the substrate.

25 A contamination produced in the machining step is, basically, an inorganic material such as abrasive or foreign matter and an organic material such as oil or

109090 6662860

fingerprints. These contaminations are produced in respective machining steps by covalent bond, electrostatic force, van der Waals power or the like. After the final surface shape and the final surface roughness of the optical element are determined, an antireflective film for improving the transmittance is formed on the surface of the substrate. Therefore, final washing after the above machining step becomes very important. In particular, with respect to, for example, an optical element for an excimer laser used in a lithography of a ultraviolet region, a very high transmittance is required. Thus, the final washing after the machining step becomes very important.

In the present invention, it is also important to remove the organic material in this washing step. However, in order to improve the transmittance of the substrate after the washing to a theoretical value, the inventor(s) considered that another light absorption factor must be removed. That is, there is, as a light absorption factor which has not been greatly studied so far, the existence of the deterioration layer produced on the surface of the CaF_2 substrate in polish-machining the substrate. In the present invention, a washing method of further removing this deterioration layer is provided to improve the transmittance of the substrate after the washing to the theoretical value.

According to a second aspect of the present

invention, as a method of removing the contamination from the surface of the substrate while keeping the crystal structure in the surface of the substrate, the surface of the substrate is processed with laser light irradiation (dry washing method) and further ultrasonic-washed with the aqueous wash solution. Here, as a laser light irradiation condition, laser light energy is set to be within a range such that CaF_2 crystal structure as material is kept.

When the surface of the CaF_2 substrate is washed by such a dry washing method, a very effective result is obtained with respect to an organic material contamination on the surface of the substrate. In this dry washing method, ultraviolet radiation with a high intensity obtained by a pulsed laser, a continuous wave laser, or a high energy lamp can be used.

In particular, when the surface of the optical element substrate is irradiated with a pulsed excimer laser, the organic material is instantly gasified and scattered from the surface of the substrate by its energy to make the washing. However, when the transmittance of the optical element is actually examined, in the case where the surface of the substrate is irradiated with, for example, KrF excimer laser light having a wavelength of 248 nm in order to make the dry washing, it is found that the transmittance of the optical element (substrate) does

not reach the theoretical value.

Thus, in this second aspect, the substrate which has been irradiated with such high energy light is further ultrasonic-washed with the aqueous wash solution for a predetermined time to improve the transmittance. When the processing is performed with the aqueous wash solution for a long time, the CaF_2 substrate is affected to deteriorate the surface and to cause a degradation in the surface roughness. Thus, this ultrasonic washing is made for a length of time which does not involve a degradation in the surface roughness to remove the deterioration layer on the surface of the substrate.

That is, the organic material adhered to the surface of the substrate is almost scattered from the surface of the substrate by the high energy light irradiation. However, the deterioration layer left on the surface of the substrate cannot be removed. Therefore, after the surface of the substrate is irradiated with high energy light, the surface of the substrate is ultrasonic-washed with the aqueous wash solution to slightly etch the surface of the CaF_2 substrate, and thus the deterioration layer is removed.

This has been ascertained by experiments as described below. In particular, when the ultrasonic washing with the aqueous wash solution is added, etching efficiency is improved. Thus, if this

processing is performed for a short time, the surface of the substrate can be etched without producing the surface deterioration of the substrate and the degradation in the surface roughness thereof. As a result, the deterioration layer left on the surface of the substrate is simultaneously removed.

First Embodiment (First Aspect)

First, as a sample, a parallel plate which is cut from the CaF_2 single crystalline substrate and has ϕ 30 \times 2t and in which both surfaces are polished is used. Note that a material in which internal absorption is 0.2% or less is used. A plurality of such substrates to be used are processed with respective different conditions and then transmittance in a wavelength of 193 nm is examined. The surface roughness is measured by an AFM measurement apparatus and an average roughness is examined with RMS. Polishing is made using diamond abrasive.

If the CaF_2 substrate is left in the air, the surface thereof is deteriorated by moisture, CO_2 , other impurities in the air. Thus, a protective film is formed after polishing. For preparation of washing, this protective film is peeled, and then the sample is immersed in acetone for two hours and pulled from the acetone. Here, both surfaces of the sample are wiped with a Clint paper containing diamond powder.

While observing the surface of the sample using a

slide star, the surface is finished with solvent (ether). Then, this sample is processed with UV/O₃. A processing time is five minutes, a distance between the surface and a light source is 30 mm, and an irradiation intensity is 12 mW/cm². With this state, the sample made of CaF₂ completely indicates hydrophilic property.

After that, the ultrasonic processing is performed with a dilution solution for two minutes, which contains a surface-active agent (neoclean, produced by Yokohama Resin) indicating alkalescent at 1%. Note that ultrasonic power is 1 kW and its frequency is 40 kHz (ultrasonic washing machine is produced by Shimada Rika Kogyo K.K.)

Further, using pure water, the ultrasonic processing is performed with the same condition as in the surface-active agent, and rinse processing is performed in pure water for 30 seconds. Then, the lens is dried with warm air to remove moisture.

With respect to the sample processed under this condition, the final transmittance at 193 nm was 92.20%. This value is equal to theoretical transmittance of CaF₂, and thus ideal cleanliness is obtained. The surface roughness of this sample was 0.5 nm (RMS). This surface roughness is not changed in comparison with the value before washing. That is, the degradation in the surface roughness by the wash etching step is not produced.

Second Embodiment (First Aspect)

As a sample, a parallel plate which is cut from the CaF_2 single crystalline substrate and has $\phi 30 \times 2t$ and in which both surfaces are polished is used. Note that a material in which internal absorption is 0.2% or less is used.

A plurality of such substrates to be used are processed with respective different conditions and then transmittance in a wavelength of 193 nm with respect to the processed respective samples is examined. The surface roughness is measured by an AFM measurement apparatus and an average roughness is examined with RMS. Polishing is made using diamond abrasive. As in First Embodiment, after a protective film is peeled, the sample is immersed in acetone for an hour and pulled from the acetone.

Here, the sample is wiped with a clint paper containing diamond powder. While observing the surface of the sample using a slide star, the surface is finished with solvent (ether). Then, this sample is processed with UV/O_3 .

A processing time is five minutes, a distance between the surface and a light source is 30 mm, and an irradiation intensity is 12 mW/cm^2 . In this state, the sample made of CaF_2 completely indicates hydrophilic property. Thus, the ultrasonic processing can be performed with a dilution solution for three minutes,

which contains a surface-active agent (neoclean,
produced by Yokohama Resin) indicating alkalescent at
0.5%. Note that ultrasonic power is 1 kW and its
frequency is 40 kHz (ultrasonic washing machine is
5 produced by Shimada Rika Kogyo K.K.).

Further, using pure water, the ultrasonic
processing is performed in same condition as in the
surface-active agent, and rinse processing is performed
with the pure water for 30 seconds. Then, the sample
10 is dried with a warm air to remove moisture. With
respect to the substrate (sample) processed under this
condition, the final transmittance at 193 nm was
92.18%. This value is approximately equal to
theoretical transmittance of CaF_2 , and thus ideal
15 cleanliness is obtained. The surface roughness of this
sample was 0.55 nm (RMS). Even in the case where the
washing is made under this condition, a reduction in
the surface roughness is not caused.

When a method of manufacturing an optical element
20 cut from the CaF_2 single crystalline substrate,
according to First and Second Embodiments described
above, is used, it can be recognized that, with respect
to the transmittance characteristic in an excimer laser
wavelength band of, in particular, a wavelength of 200
25 nm or less, good reproducibility and the transmittance
approximate to the theoretical transmittance are
obtained in comparison with a conventional case. Also,

there is an effect that use of acetone as solvent can be suppressed to very small amount. As a result, the improvement of production yield of the optical element can be expected and the optical element can be stably produced, and thus the cost can be reduced. Further, the above manufacturing method is effective in view of environmental protection.

Third Embodiment (Second Aspect)

Fig. 2 is a schematic view of a lens washing machine with laser irradiation, which is used in Third Embodiment and Fourth Embodiment described later. First, abrasive, oil content, other foreign matter, which are adhered due to the polishing process onto the surface of a lens 3 (outer diameter is 200 mm, curvature radius is 250 mm, convex lens, lens material is CaF_2) are wiped in advance to remove most soil.

Next, this lens 3 is held by a lens holder 4 in the washing machine shown in Fig. 2. In order to completely wash an effective portion of the lens, this lens holder 4 has a structure that is in contact with only rim (edge) portions of the lens 3. The lens holder 4 is supported such that it can be three-dimensionally actuated by a three dimensional control stage 5 or rotated by a rotation stage 6.

Generally, an outline of most lenses is a circle, and its shape becomes point-symmetric with the center of the lens. Thus, the lens holder 4 is rotated about

an optical axis (center axis) of the lens 3. In this embodiment, while the lens 3 is rotated at a rotation rate of 10 rpm, dry wash processing is performed.

With the lens 3 being rotated, KrF excimer laser
5 light (wavelength is about 248 nm, beam diameter is $12 \times 32 \text{ mm}^2$) with energy of 300 mJ/cm^2 is irradiated from an excimer laser apparatus (produced by Lambda Physics Co., Ltd as LPX200) composed of a light source 1 and a focal control unit 2, the irradiation position being
10 shifted at a velocity of 2 mm/sec. from the center portion of the lens 3 in the direction of the radius thereof. At this time, the height of the lens 3 in the optical axis direction is adjusted by the focal control unit 2 and the three dimensional control stage 5 such
15 that the laser beam is always focused on the surface of the lens 3. Note that a repeat frequency of the pulse laser light is 200 Hz. As described above, after the surface of the lens 3 is irradiated with the KrF excimer laser, the ultrasonic processing is performed
20 with a solution at 1 kW for two minutes, which contains a surface-active agent (semiclean, produced by Yokohama Resin) at 1% (ultrasonic washing machine is used with an oscillation frequency of 40 kHz). Then, using pure water, the ultrasonic processing is performed as
25 described above at 1 kW for two minutes. Finally, rinse processing is performed in pure water, and then drying is made with warm air to finish the surface of

09873999-060601

the lens 3.

According to examination results by a high-powered microscope, a spectroscope, or the like, it is recognized that the abrasive, the foreign matter, and the organic material residue can be almost removed. It is recognized that the final lens transmittance in 193 nm becomes the theoretical value.

Fourth Embodiment (Second Aspect)

As in Third Embodiment, first, abrasive, oil content, other foreign matter, which are adhered due to the polishing process onto the surface of a lens (outer diameter is 250 mm, curvature radius is 280 mm, concave lens, lens material is CaF_2) are wiped in advance to remove most soil. Next, this lens is held by a lens holder in the washing machine. In order to completely wash an effective portion of the lens, this lens holder has a structure that is in contact with only rim (edge) portions of the lens.

As in Third Embodiment, in the case where this concave lens is washed, since a shape of the lens is point-symmetric with the center of the lens, dry wash processing is also performed while this concave lens is rotated about the optical axis (center axis) of the lens. Also in this embodiment, this lens is rotated at a rotation rate of 10 rpm. In this state, while KrF excimer laser light (wavelength is 248 nm, beam diameter is $12 \times 32 \text{ mm}^2$) with energy of 250 mJ/cm^2 is

5

10

15

According to examination results by a high-powered microscope, a spectroscope, or the like, it is

recognized that the abrasive, the foreign matter, and the organic material residue can be almost removed.

It is recognized that the final transmittance of this concave lens becomes the theoretical value.

5 According to Third and Fourth Embodiments described above, a lens washing machine of dry washing type is used. Thus, a wash solution such as organic solvent may be greatly reduced or may be not almost used. Also, since the detergency is large, the lens
10 with very high transmittance in the ultraviolet region is obtained.

Fig. 3 is a schematic view of a projection exposure apparatus using an optical element manufactured by the manufacturing method of the present
15 invention described above as an optical system. In Fig. 3, a circuit pattern of a mask 8 is illuminated with excimer laser light having a wavelength of 193 nm or 157 nm from an illuminating optical system 7. This pattern is imaged on a wafer 10 by a projection optical
20 system 9. Note that the exposed wafer 10 is developed and processed by etching in order to manufacture a device.

As described above, the present invention can improve the transmittance of the optical element.